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Thermochimica Acta 286 (1996) 25–31

thermochimica
acta

Non-isothermal crystallization of $La_2O_3 \cdot B_2O_3 \cdot 2GeO_2$ glasses

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Received 19 October 1995; accepted 28 February 1996

Abstract

The non-isothermal crystallization of lanthanum borogermanate glasses, of stoichiometry $LaBGeO_5$ has been studied by differential thermal analysis. The phase that crystallizes during the DTA runs was identified by X-ray diffraction as the stillwellite-like $LaBGeO_5$. In the glasses studied, crystallization from surface nuclei was found to be dominant. The activation energy of crystal growth, evaluated from DTA curves, was about 465 kJ mol^{-1}.

Keywords: DTA; $LaBGeO_5$; Lanthanide borogermanate glasses; Non-isothermal crystallization; Surface nuclei crystallization; X-ray diffraction

1. Introduction

The development of glass-ceramics and glass-ceramic textures with ferroelectric and related properties poses a problem in the physics and chemistry of non-linear dielectrics as well as in electronic materials science. Information on polar glass-ceramics are limited to systems such as Li_2O–B_2O_3–SiO_2, Li_2O–ZnO–SiO_2, $Ba_2TiSi_2O_8$–$Ba_2TiGe_2O_8$, PbO–GeO_2, BaO–B_2O_3–SiO_2, and also to some perovskite-forming systems [1–9].

Recently, it has been established that La_2O_3–B_2O_3–GeO_2 stillwellite-like glass-ceramics close to the $LaBGeO_5$ composition are characterized by a number of interesting properties [10–12]. According to data in Refs. [11,12] the $LaBGeO_5$ glass-ceramics are ferroelectrics with a phase transition temperature at about 520°C.

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PII: S0040-6031(96)02935-8

They have electrical resistance over a wide temperature range, low dielectric constant and low dielectric losses. Furthermore glass-ceramic stillwellite-like textures have been synthesized recently [13,14], and the first measurement of the pyroelectric coefficient shows that its value can be more than 1 nC cm^{-2} K. Therefore the development of glass-ceramic technology on stillwellite-like textures is expedient. In connection with this a detailed study of the crystallization processes of the lanthanum borogermanate glasses has great interest.

At present experimental data on the crystallization processes of glasses of the La_2O_3–B_2O_3–GeO_2 system are poor. In accordance with data from Refs. [10–12] the stillwellite-like $LaBGeO_5$ phase is crystallized from glasses over a wide compositional range near the stillwellite stoichiometry. The authors of Refs. [11,12] suggested that surface crystallization of a stillwellite phase from the glasses melted in α-Al_2O_3 crucibles is accompanied by some bulk crystallization. At appropriate conditions [13,14] surface crystallization causes the formation of the pronounced texture whereas bulk crystallization acts counter to a texture-forming process. This hypothesis was illustrated in Ref. [13] by SEM photomicrographs reproduced in Fig. 1. However quantitative thermal analysis of the crystallization process in lanthanum borogermanate glasses has not been carried out to date. The aim of the present study was to evaluate the crystallization mechanism and the kinetic parameters for crystal growth of lanthanum borogermanate glasses of stoichiometry $LaBGeO_5$.

2. Experimental

Amounts of $La_2O_3 \cdot 3H_2O$, H_3BO_3 and GeO_2 corresponding to the composition $La_2O_3 \cdot B_2O_3 \cdot 2GeO_2$ were weighed into 20 g batches in Pt crucibles. On the basis of a previous study [10], an appropriate excess of B_2O_3 was added to compensate for its loss. The samples were melted at 1300°C. The melt was cooled by pouring into a massive metal mould and then slowly cooled from about 700°C to room temperature. Some glass pieces were disintegrated using an Al_2O_3 disk grinder.

The non-isothermal crystallization of the glass was studied by Differential thermal analysis (DTA). DTA curves were recorded in air at different heating (5, 10, 15, 20°C min^{-1}) on powders (45–63 μm) and on as-quenched bulk specimens (about 50 mg) from room temperature to 1100°C. Powdered Al_2O_3 was added to improve heat transfer between bulk samples and the sample holder. A Netzsch DSC 404 high temperature thermoanalyser was used with Al_2O_3 as reference material.

The amorphous nature of the as-quenched glass was investigated as well as the crystalline phases grown during the DTA runs. The thermally processed samples were finely ground and analysed using a computer-assisted X-ray (CuK_α) powder diffractometer (XRD), a Philips model PW 1710 diffractometer, with a scan speed of 1° min^{-1}. The X-ray diffraction patterns were matched to JCPDS data and the phases identified.

3. Results and discussion

The DTA curves, recorded at 10°C min^{-1}, of a powdered sample of the as-quenched glass (QP) and a bulk sample of the as-quenched glass (QB) are shown in Fig. 2. Both

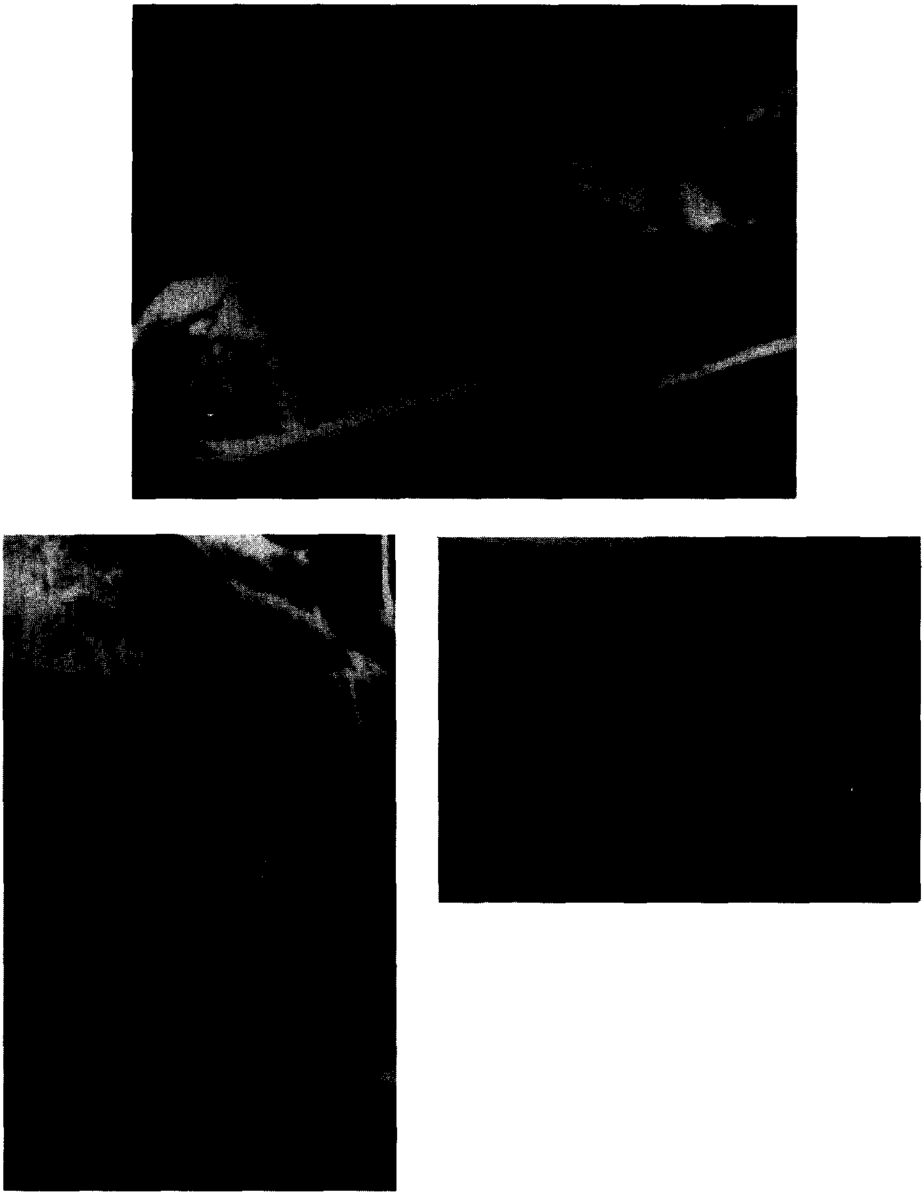

Fig. 1. SEM photomicrographs of the $LaBGeO_5$ glass samples after heat treatment at 950°C. The glass was melted in an Al_2O_3 crucible. The surface-oriented crystallization (zone A) is accompanied by some bulk crystallization (zone B). The data are from Refs. [11,12].

curves exhibit a step change in heat-flow at about 688°C that was attributed to the glass transition, followed by an exothermic peak of crystallization.

Two overlapping exothermic peaks were present in all the DTA curves of lanthanum borogermanate glasses melted in α-Al_2O_3 crucibles and quenched between metal plates

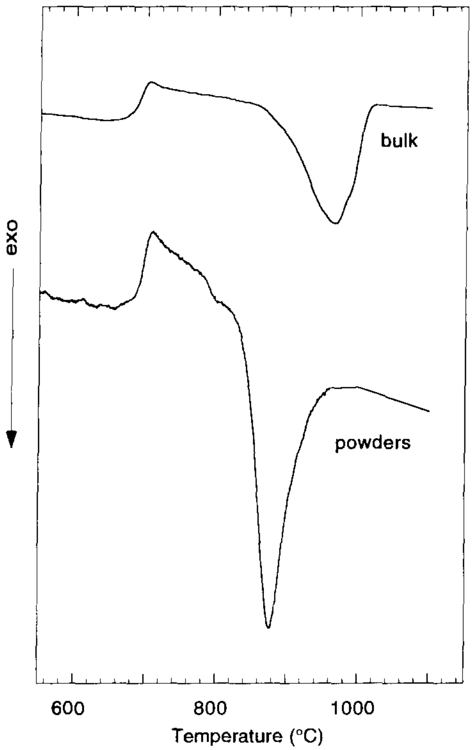

Fig. 2. DTA curves recorded in air at 10°C min^{-1} of as-quenched powders (QP) and as-quenched bulk (QB) samples.

[10,12], but the DTA curves of glasses of the same composition melted in Pt crucibles showed one exothermic peak only [13,14]. The latter is consistent with Fig. 2. The different behaviour of these glasses must be attributed to the different way of melting and quenching. It has been reported [13] that the glass melted in an α-Al_2O_3 crucible also shows some bulk $LaBGeO_5$ crystallization, see Fig. 1. However, it is evident from Fig. 1 that surface crystallization still predominates. In other words, surface crystallization is inherent to high-quality $LaBGeO_5$ glasses.

The crystalline phase that grows in the glass samples heated to the DTA exothermic peak was identified, by XRD, as $LaBGeO_5$ [10–12].

The non-isothermal devitrification of the glasses was well described by the equation proposed by Matusita and Sakka [15]:

$$-\ln(1-\alpha) = C\frac{N}{\beta^n}\exp\left(-\frac{nE}{RT}\right) \tag{1}$$

where α is the volume fraction crystallized at temperature T, β is the DTA heating rate, N is the number of nuclei per unit volume, E is the activation energy for crystal growth and C is a constant. The n parameter is related to the crystallization mechanism (surface nucleation $n = 1$, bulk nucleation $n = 3$). The higher the value of n the sharper is the DTA crystallization peak [16]. Therefore surface and bulk crystallization correspond to broad and sharp peaks, respectively.

Glass devitrification is the result of two separate processes: nucleation and crystal growth. The total number of nuclei per unit volume, N, is the sum of the surface nuclei, proportional to the specific surface area of the sample, and of bulk nuclei formed during the heat treatment [17]. The higher the number of nuclei N, the lower is the temperature of the DTA crystallization peak, T_p. Two types of crystallization can be recognized in glasses according to whether surface or bulk nucleation prevails.

The broad shape of the DTA crystallization peak, shown in Fig. 2, suggests that surface crystallization is dominant in the as-quenched glass. To check this hypothesis DTA was carried out on a finely powdered glass sample. As a consequence of the great increase in the number of surface nuclei, due to the increasing of the specific surface area of the glass sample, the DTA crystallization peak is shifted from 937 to 870°C (Fig. 2). The surface crystallization is also confirmed by the vitreous core that appears in a cross section of a bulk sample of partially crystallized glass, Fig. 3.

To verify if bulk nucleation can also occur, DTA runs were also carried out on bulk samples of glass previously heated for 16 h at 693, 723 and 743°C, a range of temperatures near the T_g where bulk nucleation rates are usually high. All these heat-treated samples showed an exothermic peak at nearly the same temperature as that of

Fig. 3. Cross-section of partially crystallized sample. Glass melted in Pt crucible.

the as-quenched glass, indicating that bulk nucleation does not occur at all or it occurs only to a very small amount.

The activation energy, E, of crystal growth has been evaluated from a set of DTA curves recorded at different heating rates on powdered (45–63 μm) samples, by use of the following equation [18]:

$$\ln\beta = -\frac{E}{RT_p} + \text{Const} \tag{2}$$

This equation is based on two assumptions: (a) at the peak temperature, T_p, the degree of crystallization reaches the same specific value and it is not dependent on the heating rate β, (b) the crystals grow at each heating rate from the same number of nuclei [17]. The value of E, 465 kJ mol^{-1}, was calculated from the slope of the straight line obtained by plotting $\ln\beta$ against $1/T_p$, Fig. 4.

A rough estimate of n was obtained by use of the following oversimplified equation [19,20], based on the assumption [21] that the ΔTdeflection of the DTA curve from the baseline is proportional to the instantaneous reaction rate at each temperature:

$$\ln\Delta T = -\frac{nE}{RT} + \text{const} \tag{3}$$

The value $n = 1.6$ was calculated from the slope of the straight line see Fig. 3, obtained by plotting $\ln\Delta T$vs. $1/T$, assuming the value of $E = 465$ kJ mol^{-1} previously determined. The above n value confirms the hypothesis that surface crystallization of the $LaBGeO_5$ glass is dominant although it is not inconsistent with the presence of a small amount of crystallization. Nevertheless, the crystallization mechanism suggested by the value of n agrees well with that deduced from the shape of the DTA peak.

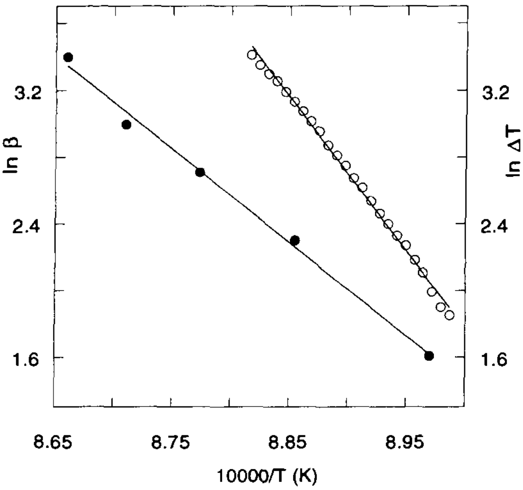

Fig. 4. Plots in $\ln\beta$ vs. $1/T_p$ (●) and $\ln\Delta T$ vs. $1/T$ (○) of as-quenched powders.

4. Conclusions

From the experimental results the following conclusions can be drawn:

(1) during a DTA run the $LaBGeO_5$ glass melted in a Pt crucible devitrifies essentially by surface nucleation;

(2) any attempt to form bulk nuclei by heat treatment in a temperature range near T_g failed;

(3) the $LaBGeO_5$ glasses melted in a Pt crucible give rise to grain-oriented glass-ceramics because the crystallization of the $LaBGeO_5$ glass in the absence of marked bulk crystallization can be a source of textured growth of stillwellite-like crystals. The latter is a major precondition for creation of ferro-pyroelectric glass-ceramic textures based on stillwellite-like phases.

Acknowledgements

This book was supported by the Russian Fundamental Research Foundation (project 95–03–08291) and by the International Science foundation.

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